

Transport Control of Eyring-Fluids along a Transversely-Corrugated Nanoannulus

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Abstract

The volume flow rates of Eyring-fluids inside the wavy-rough nanoannulus were obtained analytically (up to the second order) by using the verified model and boundary perturbation method. Our results show that the wavy-roughness could enhance the flow rate especially for smaller forcing due to the larger surface-to-volume ratio and slip-velocity effect. Meanwhile, the phase shift between the outer and inner walls of nanoannuli could tune the transport of Eyring-fluids either forward or backward when the wavy-roughness of a nanoannulus is larger enough. Our results could be applied to the flow control in nanofluidics as well as biofluidics.

PACS : 83.60.Rs, 83.50.Lh

1 Introduction

Solutions of linear chain structures exhibit interesting rheological properties such as the shear thinning and suppression of turbulent flow, which is related to flow induced changes in chain conformation and orientation. These flow properties are of great relevance in technical applications as thickeners, drag reducers, and flow improvers, as well as in the production of fiber-reinforced materials. A unique property of long chainlike molecules is the formation of entanglement networks. Already at low concentrations chain molecules start to overlap and entangle to form a transient network. Chainlike molecules subjected to a viscous shear gradient will orient in the flow, the instantaneous angular velocity being a function of the orientation relative to the local streamlines [1].

Meanwhile, researchers have been interested in the question of how some material responds to an external mechanical load [2]. External loads cause liquids to flow, in Newtonian or various types of non-Newtonian flows. Glassy materials, composed of polymers, metals, or ceramics, can deform under mechanical loads, and the nature of the response to loads often dictates the choice of material in various industrial applications. In biological systems, the response of proteins to external loads governs aspects of cell adhesion and muscle function [3]. The nature of all of these responses depends on both the temperature and loading rate. As described by Eyring [4], mechanical loading lowers energy barriers, thus facilitating progress over the barrier by random thermal fluctuations. The Eyring model approximates the loading dependence of the barrier height as linear. The Eyring model, with this linear barrier height dependence on load, has been used over a large fraction of the last century to describe the response of a wide range of systems

[5] and underlies modern approaches to biophysical rupture processes [6], sheared glasses [7], etc. To the best knowledge of the author, the simplest model that makes a prediction for the rate and temperature dependence of shear yielding is the rate-state Eyring model of stress-biased thermal activation [3,7]. Structural rearrangement is associated with a single energy barrier E that is lowered or raised linearly by an applied stress σ . In glasses, the transition rates are negligible at zero stress. Thus, at finite stress one needs to consider only the rate R_+ of transitions in the direction aided by stress.

The linear dependence will always correctly describe small changes in the barrier height, since it is simply the first term in the Taylor expansion of the barrier height as a function of load. It is thus appropriate when the barrier height changes only slightly before the system escapes the local energy minimum. This situation occurs at higher temperatures; for example, Newtonian flow is obtained in the Eyring model in the limit where the system experiences only small changes in the barrier height before thermally escaping the energy minimum. As the temperature decreases, larger changes in the barrier height occur before the system escapes the energy minimum (giving rise to, for example, non-Newtonian flow). In this regime, the linear dependence is not necessarily appropriate, and can lead to inaccurate modeling. For example, Li and Makarov [8] have shown that there is a nonlinear barrier height dependence in stretched proteins, and that the assumption of a linear dependence in the analysis of experimental results leads to inaccurate conclusions. To be precise, at low shear rates ($\dot{\gamma} \leq \dot{\gamma}_c$), the system behaves as a power law shear-thinning material while, at high shear rates, the stress varies affinely with the shear rate. These two regimes correspond to two stable branches of stationary states, for which data obtained by imposing either σ or $\dot{\gamma}$ exactly superpose. The transition from the lower branch to the higher branch occurs through a stable hysteretic loop in a stress-controlled experiment [9].

Note also that one prominent difference between the fluid motions in nanodomain and those in macrodomain is the strong fluid-wall interactions observed in nanoconduits. For example, as the nanoconduit size decreases, the surface-to-volume ratio increases. Therefore, various properties of the walls, such as surface roughness, greatly affect the fluid motions in nanoconduits.

In this short paper, we adopt the verified Eyring model [3-4] to study the transport of shear-thinning fluids within corrugated nanoannuli. To obtain the law of shear-thinning fluids for explaining the too rapid annealing at the earliest time, because the relaxation at the beginning was steeper than could be explained by the bimolecular law, a hyperbolic sine law between the shear (strain) rate : and (large) shear stress : τ was proposed and the close agreement with experimental data was obtained. This model has sound physical foundation from the thermal activation process [3-4] (Eyring [3] already considered a kind of (quantum) tunneling which relates to the matter rearranging by surmounting a potential energy barrier). With this model we can associate the (shear-thinning) fluid with the momentum transfer between neighboring atomic clusters on the microscopic scale and reveals the atomic interaction in the relaxation of flow with dissipation (the momentum transfer depends on the activation shear volume, which is associated with the center distance between atoms and is proportional to $k_B T / \tau_0$ (T is temperature in Kelvin, and τ_0 a constant with the dimension of stress)). Thus, this model could be

applied to study transport of shear-thinning fluids in nanodomain [10].

To consider the more realistic but complicated boundary conditions in the walls of nanoannulus, however, we will use the boundary perturbation technique [11] to handle the presumed wavy-roughness along the walls of nanoannuli. The relevant boundary conditions along the wavy-rough surfaces will be prescribed below.

2 Physical Formulations

We shall consider a steady transport of the (shear-thinning) fluids in a wavy-rough nanoannulus of r_2 (mean-averaged outer radius) with the outer wall being a fixed wavy-rough surface : $r = r_2 + \epsilon \sin(k\theta + \beta)$ and r_1 (mean-averaged inner radius) with the inner wall being a fixed wavy-rough surface : $r = r_1 + \epsilon \sin(k\theta)$, where ϵ is the amplitude of the (wavy) roughness, β is the phase shift between two walls, and the roughness wave number : $k = 2\pi/L$. Firstly, this fluid [3-4,10] can be expressed as $\dot{\gamma} = \dot{\gamma}_0 \sinh(\tau/\tau_0)$, where $\dot{\gamma}$ is the shear rate, τ is the shear stress, and $\dot{\gamma}_0$ is a function of temperature with the dimension of the shear rate. In fact, the force balance gives the shear stress at a radius r as $\tau = -(r dp/dz)/2$. dp/dz is the pressure gradient along the flow (or tube-axis : z -axis) direction.

Introducing $\chi = -(r_2/2\tau_0)dp/dz$ then we have $\dot{\gamma} = \dot{\gamma}_0 \sinh(\chi r/r_2)$. As $\dot{\gamma} = -du/dr$ (u is the velocity of the fluid flow in the longitudinal (z -)direction of the nanoannulus), after integration, we obtain

$$u = u_s + \frac{\dot{\gamma}_0 r_2}{\chi} [\cosh \chi - \cosh(\frac{\chi r}{r_2})], \quad (1)$$

here, u_s is the velocity over the (inner or outer) surface of the nanoannulus, which is determined by the boundary condition. We noticed that Thompson and Troian [12] proposed a general boundary condition for transport over a solid surface as

$$\Delta u = L_s^0 \dot{\gamma} (1 - \frac{\dot{\gamma}}{\dot{\gamma}_c})^{-1/2}, \quad (2)$$

where Δu is the velocity jump over the solid surface, L_s^0 is a constant slip length, $\dot{\gamma}_c$ is the critical shear rate at which the slip length diverges. The value of $\dot{\gamma}_c$ is a function of the corrugation of interfacial energy.

With the boundary condition from Thompson and Troian [12], we can derive the velocity fields and volume flow rates along the wavy-rough nanoannulus below using the verified boundary perturbation technique [11]. The wavy boundaries are prescribed as $r = r_1 + \epsilon \sin(k\theta)$ and $r = r_2 + \epsilon \sin(k\theta + \beta)$ and the presumed steady transport is along the z -direction (nanoannulus-axis direction).

Along the outer boundary (the same treatment below could also be applied to the inner boundary), we have $\dot{\gamma} = (du)/(dn)|_{\text{on surface}}$. Here, n means the normal. Let u be expanded in ϵ : $u = u_0 + \epsilon u_1 + \epsilon^2 u_2 + \dots$, and on the boundary, we expand $u(r_0 + \epsilon dr, \theta(= \theta_0))$ into

$$\begin{aligned} u(r, \theta)|_{(r_0 + \epsilon dr, \theta_0)} &= u(r_0, \theta) + \epsilon [dr u_r(r_0, \theta)] + \epsilon^2 [\frac{dr^2}{2} u_{rr}(r_0, \theta)] + \dots = \\ \{u_{slip} + \frac{\dot{\gamma}_0 r_2}{\chi} [\cosh \chi - \cosh(\frac{\chi r}{r_2})]\}|_{\text{on surface}}, \quad r_0 &\equiv r_1, r_2; \end{aligned} \quad (3)$$

where

$$u_{slip}|_{\text{on surface}} = L_S^0 \{ \dot{\gamma} [(1 - \frac{\dot{\gamma}}{\dot{\gamma}_c})^{-1/2}] \}|_{\text{on surface}}, \quad (4)$$

Now, on the outer wall (cf. [11])

$$\dot{\gamma} = \frac{du}{dn} = \nabla u \frac{\nabla(r - r_2 - \epsilon \sin(k\theta + \beta))}{|\nabla(r - r_2 - \epsilon \sin(k\theta + \beta))|}. \quad (5)$$

Considering $L_s^0 \sim r_1, r_2 \gg \epsilon$ case, we also presume $\sinh \chi \ll \dot{\gamma}_c / \dot{\gamma}_0$. With equations (1) and (5), using the definition of $\dot{\gamma}$, we can derive the velocity field (u) up to the second order : $u(r, \theta) = -(r_2 \dot{\gamma}_0 / \chi) \{ \cosh(\chi r / r_2) - \cosh \chi [1 + \epsilon^2 \chi^2 \sin^2(k\theta + \beta) / (2r_2^2)] + \epsilon \chi \sinh \chi \sin(k\theta + \beta) / r_2 \} + u_{slip}|_{r=r_2+\epsilon \sin(k\theta+\beta)}$. The key point is to firstly obtain the slip velocity along the boundaries or surfaces. After lengthy mathematical manipulations, we obtain the velocity fields (up to the second order) and then we can integrate them with respect to the cross-section to get the volume flow rate (Q , also up to the second order here) : $Q = \int_0^{\theta_p} \int_{r_1+\epsilon \sin(k\theta)}^{r_2+\epsilon \sin(k\theta+\beta)} u(r, \theta) r dr d\theta = Q_{slip} + \epsilon Q_{p_0} + \epsilon^2 Q_{p_2}$. In fact, the approximate (up to the second order) net volume flow rate reads $Q \equiv Q_{out} - Q_{in}$ which is the flow within the outer (larger) wall : Q_{out} without the contributions from the flow within the inner (smaller) wall Q_{in} .

3 Results and Discussions

We shall demonstrate our results below. The wave number of roughness is fixed to be 10 (presumed to be the same for both walls of the nanoannulus) for all figures here. Firstly, there is an enhanced flow rate once the wavy-roughness is increasing [10]. This enhancement is rather significant especially when the forcing (along the annulus-axis direction : χ / r_2) is absent or zero (purely slip flow). As the annulus size decreases, the surface-to-volume ratio increases. Therefore, surface roughness along both walls together with the slip-velocity boundary condition, greatly affect the fluid motions between the corrugated nanotubes.

Not that for an easy comparison, we select the parameters to be $r_2 = 2, r_1 / r_2 = 0.5, L_s^0 / r_1 = 1; \dot{\gamma}_0 / \dot{\gamma}_c = 0.1$. For rather weakly corrugations : $\epsilon = 0.06 r_1$ the flow rate is monotonically decreasing for χ / r_2 around 5. However, once we increase χ / r_2 to be around 7, the flow rate will be monotonically increasing. Q (the net volume flow rate) will firstly decrease to a minimum and then keep increasing monotonically. This behavior is almost the same for β (phase shift) being equal to $\pi/4, \pi/2$ and π (however, the effect of phase shift is minor for very-small wavy-roughness [10]). It seems to us that, however, for very-small applied forcing there is a barrier manifested by the shearing (of fluids along wavy-rough surfaces) which leads to a minimum flow rate. As the forcing is large enough and the barrier can be overcome then the transport (of fluids) keeps increasing. The latter is something like a tunneling process [3-4]!

To examine the realistic effects of phase shift (β) between the outer-wall wavy-roughness and the inner-wall one, we fix the outer-wall and the inner-wall radii (to be 1 and 0.6 nm, respectively). The small amplitude of wavy-roughness of both walls is also fixed to be $0.06 r_1$. We consider two cases : $\beta = \pi/4, \pi$ for the same $\dot{\gamma}_0 = 10000.0 \text{ (s}^{-1}\text{)}$ (cf. [14]) with $\dot{\gamma}_0 / \dot{\gamma}_c = 0.1$. The results are

illustrated in Fig. 2. We observe that for $\beta = \pi/4$ the net volume flow rate $Q \equiv Q_{out} - Q_{in}$ is decreasing as the forcing increases (starting from zero but within a small range). The trend for $\beta = \pi$, however, reverses! Q for $\beta = \pi$ is monotonically increasing and positive for larger forcing. Here, the interesting observation is for small applied forcing ($4.5 \leq \chi/r_2 \leq 7.5$, r_2 is fixed to be unity), once $\beta = \pi/4$, the flow moves backward (along the annulus-axis direction, even though the flow still moves forward once $\chi/r_2 \geq 8$ [14] as also evidenced in Fig. 1 since there is a minimum flow rate for larger wavy-roughness for certain χ/r_2 under selected geometry). This result thus could be applied to the flow control in nanofluidics.

In brief summary, we have theoretically obtained the volume flow rates (up to the second order) of Eyring-fluids inside the wavy-rough annular nanotubes by using the verified fluid model [3-4,10] and boundary perturbation method [11]. Our results show that the wavy-roughness could tune the flow rate especially for smaller forcing due to the larger surface-to-volume ratio and slip-velocity effect. Meanwhile, the phase shift between the outer and inner walls of nanoannuli could tune the transport of shear-thinning fluids either forward or backward when the wavy-roughness is larger enough as illustrated in Figure 2 here. Our results could be applied to the flow control in nanofluidics [15] as well as biofluidics [1].

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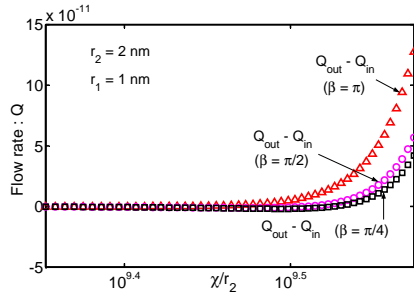


Fig. 1 Calculated net volume flow rates (Q) w.r.t. χ/r_2 (forcing (along the z -axis direction) per unit volume and referenced shear stress). The mean outer radius is $r_2 = 2$ (nm), and the mean inner one is $r_1 = 1$ (nm). The slip length reads $L_s^0 = r_1$. ϵ ($=0.06 r_1$ here) is the amplitude of wavy roughness. The wave number of roughness (k) is 10 here. We demonstrate the effects of wavy-roughness via its phase shift β ($=\pi/4, \pi/2, \pi$ here) between the outer and inner walls of a nanoannulus. For smaller β , Q is smaller w.r.t. the same χ/r_2 (forcing). Meanwhile there is a minimum flow rate (corresponds to a barrier). The unit of volume flow rate is m^3/s .

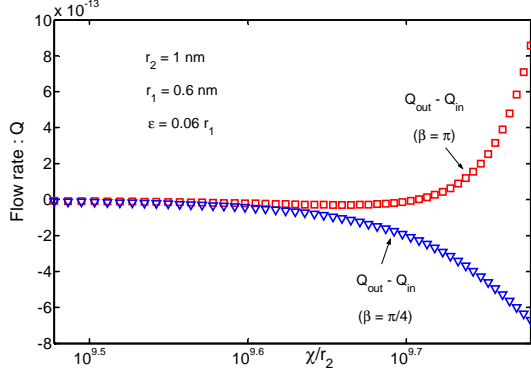


Fig. 2 Calculated volume flow rates (Q) w.r.t. χ/r_2 (forcing (along the z -axis direction) per unit volume and referenced shear stress) for different phase shifts (β s). The mean outer radius $r_2 = 1$ nm, and the mean inner radius $r_1 = 0.6$ nm. The amplitude of wavy-roughness ϵ ($=0.06 r_1$ here) is enlarged here and the wave number of roughness (k) is 10 here. We consider two phase shifts ($\beta = \pi/4, \pi$) and the effect is significant for the range of χ/r_2 here. The unit of volume flow rate is m^3/s . Q for $\beta = \pi/4$ is monotonically decreasing (up to dimensionless $\chi/r_2 \geq 8$ as r_2 is unity) and there is backward transport for this case. The trend for $\beta = \pi$ reverses. This result could be applied to the flow control in nanofluidics.